



US010125020B2

(12) **United States Patent**
Estenfelder et al.

(10) **Patent No.:** **US 10,125,020 B2**
(45) **Date of Patent:** ***Nov. 13, 2018**

(54) **AMMONIA OXIDATION CATALYSTS**
(71) Applicant: **SUED-CHEMIE CATALYSTS**
ITALIA S.R.L., Novara (IT)
(72) Inventors: **Marvin Estenfelder**, Novara (IT);
Alberto Cremona, Castell'Arquato (IT)
(73) Assignee: **SUED-CHEMIE CATALYSTS**
ITALIA S.R.L., Novara (IT)
(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 112 days.
This patent is subject to a terminal dis-
claimer.

(21) Appl. No.: **13/770,351**

(22) Filed: **Feb. 19, 2013**

(65) **Prior Publication Data**
US 2013/0164494 A1 Jun. 27, 2013

Related U.S. Application Data
(63) Continuation of application No. 12/640,266, filed on
Dec. 17, 2009, now Pat. No. 8,435,917.

(30) **Foreign Application Priority Data**
Dec. 23, 2008 (EP) 08172820

(51) **Int. Cl.**
C01B 21/26 (2006.01)
B01J 35/10 (2006.01)
B32B 3/12 (2006.01)
C01B 21/28 (2006.01)
B01J 23/89 (2006.01)
B01J 19/24 (2006.01)
B01J 35/04 (2006.01)
B01J 37/02 (2006.01)

(52) **U.S. Cl.**
CPC **C01B 21/265** (2013.01); **B01J 19/2485**
(2013.01); **B01J 23/8986** (2013.01); **B01J**
35/10 (2013.01); **B01J 37/0248** (2013.01);
B32B 3/12 (2013.01); **C01B 21/28** (2013.01);
B01J 35/04 (2013.01); **B01J 37/0205**
(2013.01); **B01J 37/0207** (2013.01); **Y10T**
428/24149 (2015.01)

(58) **Field of Classification Search**
CPC C01B 21/265; C01B 21/28; B32B 3/12;
B01J 35/10; B01J 35/04; B01J 23/8986;
B01J 19/2485; B01J 37/0248; B01J
37/0205; B01J 37/0207; B01J 19/24;
C04B 38/0006; C04B 38/0016
See application file for complete search history.

(56) **References Cited**
U.S. PATENT DOCUMENTS
4,820,678 A 4/1989 Xu
4,912,776 A 3/1990 Alcorn
4,963,521 A 10/1990 Engler et al.
5,217,939 A 6/1993 Campbell
5,690,900 A * 11/1997 Smojver B01J 23/83
423/392
6,451,278 B1 9/2002 Zolotarsky et al.
6,827,917 B1 12/2004 Ward et al.
7,722,845 B2 5/2010 Caudle et al.
2003/0083198 A1 * 5/2003 Xu B01J 8/0415
502/20
2006/0182676 A1 8/2006 Tran et al.
2006/0204415 A1 * 9/2006 Jiang C01B 3/386
422/211
2006/0216467 A1 9/2006 Yoshida
2007/0261557 A1 * 11/2007 Gadkaree B01D 53/02
96/121
2008/0075655 A1 3/2008 Davydov et al.
2010/0113244 A1 5/2010 Chi et al.

FOREIGN PATENT DOCUMENTS

GB 2 406 802 A 4/2005
WO 98/28073 7/1998
WO 99/25650 5/1999
WO 2006/009453 1/2006
WO 2008/090450 7/2008

OTHER PUBLICATIONS

Chinese Patent Application Publication No. 86/108985, dated Apr.
20, 1988 (Abstract only).
U.S. Official Action dated Jun. 15, 2011 in related U.S. Appl. No.
12/640,266.
U.S. Official Action dated Nov. 14, 2011 in related U.S. Appl. No.
12/640,266.
U.S. Official Action dated Jun. 7, 2012 in related U.S. Appl. No.
12/640,266.

* cited by examiner

Primary Examiner — Anthony J Zimmer
(74) *Attorney, Agent, or Firm* — Scully, Scott, Murphy &
Presser, P.C.

(57) **ABSTRACT**

Ammonia oxidation catalyst units comprising a pair of
honeycomb-type blocks having interplaced between them a
layer of a gas permeable material performing the function of
radially mixing the gas flow, said blocks comprising an
ammonia oxidation catalysts, and having height of less than
15 cm and the interplaced layer height of 3 to 0.5 cm.

6 Claims, No Drawings

AMMONIA OXIDATION CATALYSTS

RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 12/640,266, filed Dec. 17, 2009, the entire content and disclosure of which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

The present invention relates to an ammonia oxidation catalyst unit formed of a pair of honeycomb-type blocks comprising an ammonia oxidation catalyst and having inter-
placed between them a layer of foamed material.

For many years, the catalysts for ammonia oxidation have been formed of meshes or gauzes of platinum or its alloy with other precious metals.

Such catalysts have good activity and selectivity but suffer from the disadvantage that the catalyst is not only very expensive but also it exhibits an appreciable loss of platinum at the high temperatures of the oxidation reaction with consequent low catalyst life, which requires frequent replacement.

It is therefore desirable to provide a replacement of such precious metal catalyst.

It is well known that oxides of metals such as manganese, iron, nickel or, especially cobalt, often used in conjunction with one or more rare earth metal oxides, exhibit activity for ammonia oxidation.

CN-A-86/108 985 describes a catalyst composition of formula $La_{1-x}CeCoO_3$ (where x is a number from 0 to 1) having perovskite structure, endowed with good activity and selectivity when tested on small scale, which decreases when operating at temperatures (800°-1000° C.) normally employed for ammonia oxidation.

U.S. Pat. No. 4,963,521 describes an exhaust gas catalyst which, in one embodiment, is formed of honeycomb cordierite coated with a first layer of gamma alumina mixed with minor proportion of zirconia and ceria, and a second layer formed of cobalt oxide or platinum, rhodium and palladium.

No mention is made that the catalyst can be used for oxidizing ammonia.

U.S. Pat. No. 5,217,939 describes an ammonia oxidation catalyst obtained by coating a reticulated foamed ceramic or metal substrate with cobalt oxide or with a noble metal.

The coating is obtained by immersion of the foamed substrate in a solution of a carboxylate of cobalt, or of a noble metal, removing the substrate from the solution and calcinating at temperatures from 260° to 800° C. (at which the cobalt carboxylate is converted into oxide and the carboxylate of the noble metal is reduced to the metal).

The ceramic foams have a number of pores per linear inch of 10 to 100 (4-40/cm); 30 pores in the examples.

The conversion of ammonia to NO using the foam-Co oxide coated is 92-95%; using the foam coated with Pt 97-100%.

Further processing is necessary to convert nitric oxide (NO to NO₂) and then to nitric acid.

More efficient and economical catalysts in the production of nitric acid are therefore needed.

More efficient catalysts producing relatively high yields of NO₂ are described in U.S. Pat. No. 5,690,900. The catalysts are formed of porous ceramic (200-600 cells per square inch i.e. 14-24 cells per linear inch=5-9 cells/cm) coated with at least three layers: the first is formed of

alumina with minor proportion of ceria and zirconia, the second of oxides of cobalt, zirconium and cerium, the third of platinum metal.

The layers are obtained by immersing the porous ceramic body in a suspension of alumina, zirconium oxide and cerium nitrate, removing the impregnated ceramic structure and calcinating at 600° to 1000° C.

The resulting surface area is 80-120 m²/g.

The thus coated ceramic is then immersed in a solution of cobalt acetate, cerium nitrate and zirconium acetate, removed from the solution, and calcinated at 600-1000° C.

The last layer is obtained by immersion in a solution of platinum oxalate, and calcination at 600-1000° C. of the structure removed from the solution of the previous treatment.

The ammonia conversion to NO/NO₂ is 95-100% with NO/NO₂ ratio of 75/25 to 60/40.

U.S. Pat. No. 4,820,678 describes honeycomb-like alloy tapes coated with a catalyst having the perovskite (ABO₃) or spinel (A₂BO₄) structure, wherein A comprises cations of rare earth metal, B, in the perovskite structure, is selected from manganese, copper and nickel cations, in the spinel structure is selected from iron and nickel.

The catalyst is used for the purification of industrial waste gases, exhaust gases from automobiles, and purification of air.

The honeycomb tapes are obtained by perforating Fe—Cr—Al or Fe—Ni—Al alloy strips of about 0.05-0.12 mm thickness at distance of about 1.1-1.2 mm apart to form small holes of 0.4×0.4 mm.

OBJECTS

It is an object of the present invention to provide ammonia oxidation catalysts comprised in honeycomb-type structures (wherein, due to their tubular structure, no radial gas flow mixing occurs and therefore no satisfactory conversion of the reagents) capable of giving high catalyst performance in terms of activity and selectivity and high specific productivity referred to the volume of the honeycomb structure bed and the weight of the catalyst.

SUMMARY OF THE INVENTION

The ammonia oxidation catalysts of the present invention are formed of one or more unit structures each of which formed of a pair of blocks having honeycomb-type structure comprising catalyst material, the blocks having interplaced between them a layer of gas permeable material wherein a radial mixing of the reagent gas flow is obtained.

DETAILED DESCRIPTION OF THE INVENTION

The blocks have height of not more than 15 cm, preferably not more than 10 and more preferably not more than 6 cm and more than 2 cm. The height of the interplaced layer is more than 0.5 cm and not more than 3 cm preferably not more than 2 cm.

A foamed material having open, randomly connected cells is usable to form the interplaced layer.

For honeycomb-type structure it is meant a structure formed of tubular not interconnected through bores.

As indicated, in the above structure the interplaced layer performs the function of thoroughly mixing the gas flow exiting the first honeycomb block wherein, due to laminar piston-type flow inside the tubular not interconnected

through bores, no radial mixing occurs, thus allowing better conversion inside the second block.

The laminar piston-type flow inside the tubular through bores of the blocks favors the maintenance of constant reagents concentration at contact with the catalyst covering the walls of the through bores.

The material of honeycomb-type block preferably is ceramic or metallic; any other material resistant to the high temperatures of the ammonia oxidation reaction can also be used. For example, the material of the honeycomb type block can be a perovskite of the ABO_3 type wherein A is a rare earth-element or an alkaline-earth element or mixtures thereof and B is a transition metal element or mixtures thereof.

The density of the cells ranges from 3 to 10 cells/cm; that of the pores of the foamed material is of 4 to 20/cm.

Commercial honeycomb-type blocks are available from Emitech-Germany; commercial foams from Hi-Tech Ceramics—NY, USA.

Foamed alpha alumina and reticulated foams with open cells randomly connected are preferred.

Usable honeycomb-type alloy blocks can also be obtained from tapes prepared according to U.S. Pat. No. 4,820,678.

Any type of ammonia oxidation catalyst can be used in the honeycomb-type structure unit according to the invention. The final catalyst can be obtained by either

- a) coating an inert honeycomb monolithic structure with the active element or
- b) extruding the active element powder to a honeycomb monolithic type structure.

A preferred catalyst comprises mixed oxides of cobalt, manganese and rare earth metals having composition expressed as percentage by weight of Co O, Mn O and rare earth oxide in the lowest state of valence as follows: 20-45% Co O, 50-60% Mn O, 0.5-20% rare earth metal oxide, preferably La_2O_3 and its mixtures with CeO_2 . The mixed oxides are supported on porous inorganic metal oxides, preferably gamma alumina. Catalysts of this type containing Cu O in place of Co O, and the preparation thereof are described in WO 2008-090450.

Examples of other usable catalysts are described in U.S. Pat. Nos. 5,217,939 and 5,690,900, and WO 99/25650. Other examples are the perovskite type catalyst (ABO_3) and the spinel type (AB_2O_4).

The catalyst unit allows to obtain high conversion of ammonia to NO.

The oxidation reaction conditions are: temperature from 200° C. to 900° C., pressure 1 to 12 bar abs., GHSV 8.000-140.000 h^{-1} .

The unit, thanks to its specific structure offers advantages with respect to the back pressure and increases the space-time yield since the throughput of the existing plants can be more heavily loaded.

Example 1

A catalyst unit formed of three units of honeycomb-like structure ceramic blocks each having 5 cm height, 62 cells/cm² and including two layers of foamed alfa alumina each 2 cm thick interplaced by alternating one block of monolith and one foam until the five structures are arranged in cascade, was prepared by immersing the blocks in a slurry containing gamma alumina milled to 1 to 10 μm having supported on it a mixed oxides catalyst of composition expressed in percentage by weight of Co O, Mn O and La_2O_3 of 37.4% Co O, 53.4% Mn O and 9.2% La_2O_3 . The supported catalyst comprised also Pt in amount of 0.1-0.2 wt

%. Said transition metal oxides are supported on gamma alumina in a global amount equal to 20% by weight. The slurry is further composed of deionized water and made acidic to pH 4 with acetic acid.

The catalyst was prepared by impregnating gamma alumina with an aqueous solution of lanthanum nitrate ($La(NO_3)_3$).

The impregnated support was then dried at 110° C., calcined at 600° C. and thereafter impregnated with an aqueous solution of manganese nitrate ($Mn(NO_3)_2$), cobalt nitrate ($Co(NO_3)_2$) and $Pt(NH_3)_4 Cl_2$, and dried at 120° C.

A volume of solution equal to 100% of the pore volume of alumina was used for impregnation.

The immersed blocks were removed from the slurry and calcinated at 500° C. to obtain reduction of platinum ions to metal.

The thus obtained unit was inserted into a reactor for ammonia oxidation. The reaction conditions were: GHSV=10.000 h^{-1} , temperature of the gas mixtures taken at the inlet of the catalyst unit 550° C., pressure 1 bar and ammonia concentration equal to 1% v/v in air.

The conversion of ammonia to NO was higher than 96%.

Comparison Example 1

A catalyst unit similar to that used in Example 1, but not comprising the foamed alumina layers, was used in a test of ammonia oxidation carried out under the same conditions as in Example 1.

The conversion of ammonia to NO was 87%.

Comparison Example 2

A catalyst unit formed of a single honeycomb-like structure ceramic block having 15 cm height, 62 cells/cm² was prepared according to the procedure already described in the EXAMPLE 1 and was used in a test of ammonia oxidation carried out under the same conditions as in Example 1.

The conversion of ammonia to NO was 74%.

The disclosures in European Patent Application No. 08172820 from which this application claims priority are incorporated herein by reference.

What is claimed is:

1. A catalyst for ammonia oxidation formed of one or more catalytic units each of which is formed of a pair of blocks having a honeycomb structure containing tubular passages not interconnected through bores, comprising: an ammonia oxidation catalyst, each of said blocks having a height between 2 cm and 15 cm and interplaced between the pair of blocks a foamed layer having a height between 0.5 cm and 3 cm, formed of foamed material having open, randomly connected cells wherein the ammonia oxidation catalyst is obtained by coating with at least three layers, the first layer comprising alumina, ceria and zirconia, the second layer comprising oxides of cobalt, zirconium and cerium, and the third layer comprising platinum metal.

2. The catalyst according to claim 1, wherein both the ceria and the zirconia of the first layer are in a smaller proportion as compared to the alumina of the first layer.

3. A honeycomb structure formed of one or more units each of which is formed of a pair of blocks having tubular passages not connected through bores, each of said blocks having height of less than 6 cm and more than 5 cm and interplaced between them a layer of foamed material having randomly connected cells, said layer having a height of less than 2 cm and more than 0.5 cm, wherein each of said blocks can be coated with a catalyst suitable to oxidize ammonia.

5

6

4. The honeycomb structure according to claim 3, wherein the density of cells of the foamed layer ranges from 3 to 10 cells/cm.

5. The honeycomb structure according to claim 3, wherein the blocks are formed of ceramic or metallic material. 5

6. The honeycomb structure according to claim 3, wherein the blocks have a number of cells per cm, which can be the same or different, from 3 to 10 and wherein the number of pores per cm of the foamed layer is 4 to 20.

* * * * *

10